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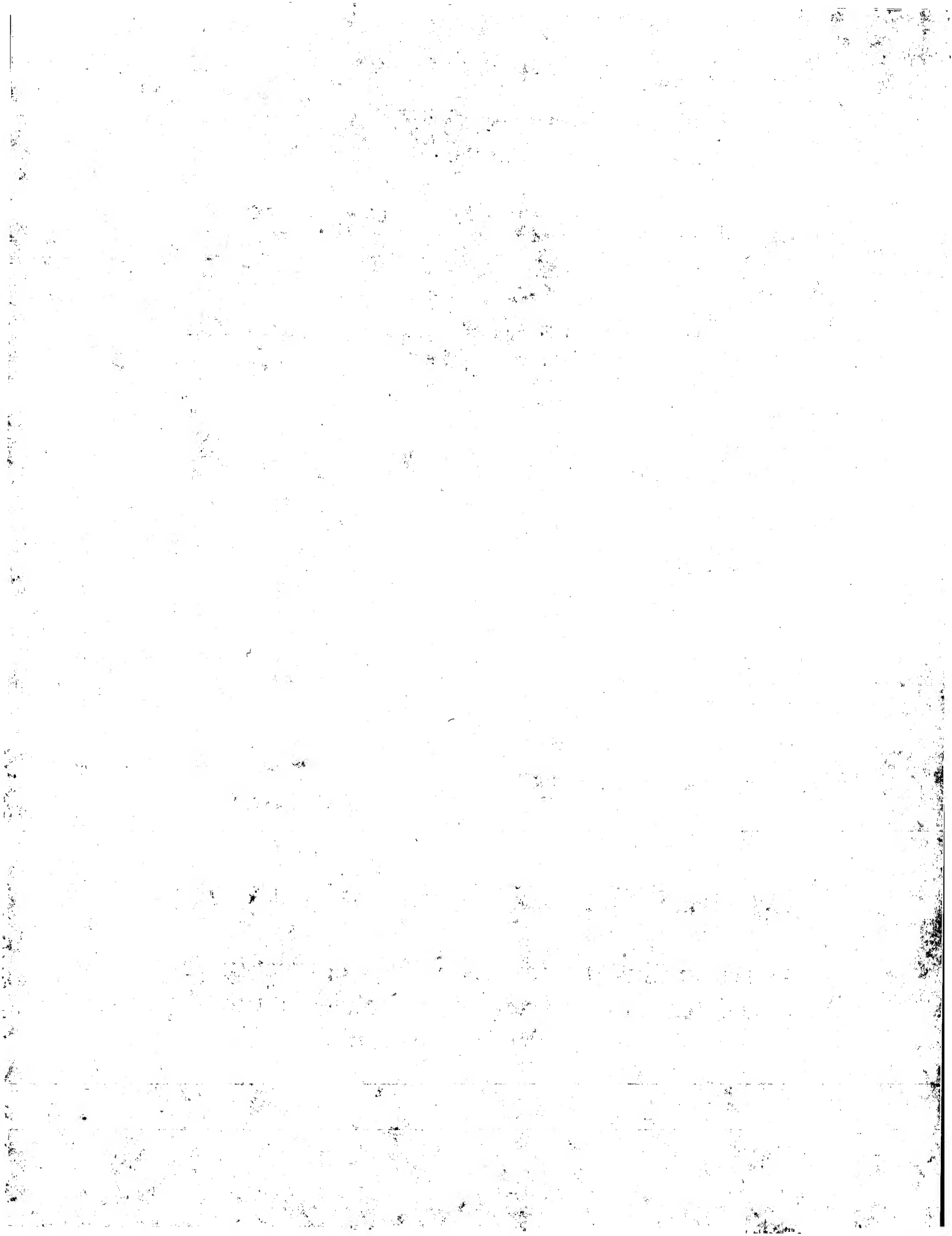
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(54) Title: POLYVINYL ACETAL COPOLYMERS AND THEIR PREPARATION (57) Abstract Random copolymers of vinyl acetal with comonomers having lactone or carboxylate-salt groups are disclosed. Such copolymers may exhibit improved water solubility compared to polymers of equivalent acetalization levels lacking the comonomers.		

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TITLE**POLYVINYL ACETAL COPOLYMERS AND THEIR PREPARATION****FIELD OF INVENTION**

5 Polyvinyl acetal copolymers comprising lactone or carboxylate-salt functionalities, including copolymers exhibiting improved water solubility, are disclosed.

BACKGROUND OF THE INVENTION

10 Polyvinyl acetals are tough, chemically resistant polymers that exhibit strong adhesion to a wide variety of surfaces. Because of these properties, polyvinyl acetals are useful in coatings and are often used as an interlayer in safety glass.

Preparation of polyvinyl acetals by the reaction of a polyvinyl alcohol with an aldehyde is well known in the art. See, for example, U.S. Patent No. 4,747,976 and 4,990,335. In general, see "Acetalization of Polyvinyl Alcohol" by K. Toyoshima, Chapter 15, pp. 391-411 of Polyvinyl Alcohol Properties and Applications, C. A. Finch, Ed. (John Wiley & Sons Ltd., London, England 1973). More recent references to polyvinyl acetals are "Developments in the Production and Applications of Polyvinyl Butyral and Other Polyvinyl Acetals" by K. Asahina, Chapter 19, pp. 673-688 of Polyvinyl Alcohol - Developments, C. A. Finch, Ed. (John Wiley & Sons Ltd., Chichester, England 1992); and "Vinyl Acetal Polymers" by T. P. Bloomstrom, which is contained in Encyclopedia of Polymer Science and Engineering, Volume 17, J. L. Kroschwitz, Ed. (John Wiley & Sons Ltd., New York and Chichester 1989), pp. 136-167.

25 German Patent 690,349 discloses compositions, useful in preparing safety glass, containing polyvinyl acetals, especially formaldehyde polyvinyl acetal, which polyvinyl acetals may also incorporate plasticizers, cellulose derivatives, poly(vinyl esters), or poly(acrylate esters).

30 It is generally recognized within the art that the water solubility of a polyvinyl acetal material decreases with increasing acetalization levels. For example, polyvinyl butyrals become water-insoluble at acetalization levels of ten or more mole percent. For use in water based coatings or as water soluble packaging films, polyvinyl acetals with greater water solubility at high levels of acetalization are desirable.

Water-soluble polyvinyl-acetal materials are known. U.S. Patent No. 5,135,982 discloses a water-soluble packaging film consisting of a polyvinyl-acetal polymer formed by acetalizing to an acetalization degree of 1-30 mole percent a copolymer of polyvinyl alcohol and benzaldehyde derivatized with a sulfonic acid or sulfonic acid salt functionality. U.S. Patent No. 5,019,624

discloses water-soluble polyvinyl-acetal articles composed of a polyvinyl alcohol acetalized with terminally etherified oxyethylene aldehydes/oxaalkanals such as 3,6-dioxahexanal. Japanese Patent Publication Number 2914/1957 discloses polyvinyl alcohol fibers which are acetalized with aldehydes that incorporate a
5 carboxylic-acid group, such as chlorophthalic aldehyde, phthalic acid aldehyde, or adipic acid aldehyde. Japanese Patent Publication Number 4012/1961 discloses polyvinyl alcohol materials acetalized with aldehydes that incorporate acid groups, such as glyoxylic acid, carboxyacetaldehyde, or sulfobenzaldehyde. European Patent Application Number 0 530 591 A1 discloses water-absorptive
10 fibers composed of ethylene/vinyl-alcohol copolymers acetalized with aldehydes that incorporate carboxylic acids or carboxylic acid salts.

Japanese Patent Application 61-130,349 discloses porous polymeric materials produced from block copolyvinyl acetals. Said block copolyvinyl acetals may include comonomers derived from, for example, methacrylic acid,
15 methacrylamide and the like.

U.S. Patent No. 4,747,976 discloses random copolymers of polyvinyl alcohol and vinyl esters as well as copolymers of polyvinyl alcohol with lactones and copolymers of polyvinyl alcohol with carboxylate ionomers.

SUMMARY OF INVENTION

20 This invention relates to a random polyvinyl-acetal copolymer that comprises from 90 to 99 mole percent vinyl-alcohol repeat units and from 1 to 10 mole percent monomers with lactone functionalities or carboxylate-salt functionalities, wherein the copolymer has an acetalization degree of between 1 to 80 percent of the vinyl-alcohol repeat units.

25 In a preferred embodiment of this invention, such a polyvinyl-acetal copolymer has an acetalization degree of between 5 and 25 percent of the vinyl alcohol repeat units. Such a copolymer exhibits increased water solubility compared to a polyvinyl alcohol having a comparable level of acetalization but not incorporating the lactone functionalities or carboxylate-salt functionalities.

30 This invention further provides a process for making random polyvinyl acetal copolymers which incorporate from 90 to 99 mole percent vinyl alcohol units and from 1 to 10 mole percent lactone functionalities or carboxylate-salt functionalities, with an acetalization degree of from 1 to 80 percent of the vinyl alcohol units, comprising reaction by mixing, in a suitable liquid medium,
35 polyvinyl-alcohol/lactone copolymer with an aldehyde in the presence of optional acid catalyst in the range of 0-100°C, followed by neutralization either a weakly alkaline solution, to obtain lactone functionalities, or a strongly alkaline solution to obtain carboxylate-salt functionalities.

The random polyvinyl acetal copolymers of this invention are useful as water-soluble packaging film, for example, to contain alkaline or acidic materials such as soaps, laundry detergents, bleaching agents, agrochemicals, pigments, dyes, and industrial chemicals. The random polyvinyl acetal copolymers of this invention are also useful as binders for pigments or ceramic powders, for the preparation of inks, hot-melt adhesives, adhesives, coatings and the like.

DETAILS OF INVENTION

As mentioned above, this invention relates to random polyvinyl acetal copolymers which incorporate from 90 to 99 mole percent vinyl alcohol units and from 1 to 10 mole percent lactone functionalities or carboxylate-salt functionalities, with an acetalization degree of from 1 to 80 percent of the vinyl alcohol units.

In one preferred embodiment of the invention, the random polyvinyl-acetal/lactone copolymers of this invention exhibit enhanced water solubility compared to polyvinyl-acetal polymers of comparable acetal concentration but lacking the monomer providing the lactone or carboxylate-salt functionality.

It has been found that the water solubility of the polymers of this invention may depend upon the relative concentrations of lactone functionality. In general, for acetal levels below 5 mole percent, the presence of lactone in the 1-10 mole percent range has little effect on the already highly soluble polymer. At acetal levels in the range of 5 mole percent to 25 mole percent, incorporation of lactone has the effect of increasing the solubility of the polymer by 2.5 to 150 percent, depending upon the specific concentrations of each comonomer unit within a suitable range for the practice of this invention.

Another embodiment of this invention comprises random polyvinyl-acetal/carboxylate-salt copolymers comprising 5-25 mole percent acetal and from 1-10 mole percent carboxylate-salt functionality. The random polyvinyl-acetal/carboxylate-salt copolymers of this invention have been discovered to exhibit enhanced water solubility compared to polyvinyl acetal polymers of comparable acetal concentration but lacking the carboxylate comonomer.

It is found in the practice of this invention that the water solubility of the polymers of this invention depends upon the relative concentrations of acetal and carboxylate-salt functionality. At acetal levels in the range of 5 mole percent to 25 mole percent, incorporation of the carboxylate salt has the effect of increasing the solubility of the polymer by 2 to about 70,000 percent, depending upon the specific concentrations of each comonomer unit within a suitable range for the practice of this invention.

While the exact dependency of polymer solubility on acetal and/or comonomer concentrations is illustrated in the specific embodiments hereinbelow provided, it is in general found that at the lower end of the acetal range hereinabove specified, less carboxylate or less lactone is required to achieve a given level of water-solubility than at the higher end of the acetal range.

In a first process according to the present invention, random polyvinyl-acetal/lactone copolymers are prepared by acetalization of random polyvinyl-alcohol/lactone copolymers that are known in the art. Polyvinyl alcohol is typically produced by hydrolysis of polyvinyl acetate, as described in the references cited above. In the parlance of the art, and as herein practiced, the total concentration of both hydrolyzed and unhydrolyzed acetate groups is referred to as "vinyl alcohol," with the amount of acetate actually converted to vinyl alcohol indicated as the "% hydrolyzed". Suitable for the use as a starting material for this process are random polyvinyl-alcohol/lactone copolymers comprising 90 to 99 mole percent vinyl alcohol and 1 to 10 mole percent ester-containing comonomer units. The random polyvinyl-alcohol copolymer compositions which incorporate the ester-containing units should have an hydrolysis level of from 50.0 to 100.0 mole percent, preferably at least 75.0 mole percent, most preferably 95.0 to 100.0 mole percent.

It will be readily appreciated by the skilled artisan that the ester-containing units incorporated within the polyvinyl-alcohol copolymers of the present invention can take the form of an internal lactone function. The random polyvinyl-alcohol/lactone copolymers suitable for this process may be produced by any convenient method known in the art. For example, the random polyvinyl-alcohol/lactone copolymers suitable for use as a starting material may be produced as taught in U.S. Patent No. 4,747,976 and U.S. Patent No. 4,990,335.

The ester-containing comonomer units suitable for incorporation into the polyvinyl-acetal/lactone copolymers of this invention may be derived from lower alcohol esters of acrylic acid, for example, methyl acrylate, ethyl acrylate, propyl acrylate and the like; lower alcohol esters of methacrylic acid, for example, methyl methacrylate, ethyl methacrylate, propyl methacrylate and the like; lower alkyl diesters of maleic acid, for example, dimethyl maleate, diethyl maleate, dipropyl maleate, and the like; lower alkyl diesters of fumaric acid, for example, dimethyl fumarate, diethyl fumarate, dipropyl fumarate and the like, or mixtures thereof. These examples should not be considered limiting. Essentially any ester-containing unit, which may be copolymerized with vinyl acetate to form random polyvinyl-acetate copolymers within the specified levels described above, may

find utility within the present invention. Methyl methacrylate, methyl acrylate, or mixtures thereof are preferred, however, for the practice of this invention.

Suitable aldehydes for the acetalization reaction of this process include aliphatic aldehydes, aliphatic-aromatic aldehydes, aromatic aldehydes, terminally etherified oxyethylene aldehydes/oxaalkanal, and mixtures thereof. Again, these examples should not be considered limiting. Essentially any aldehyde which can be acetalized with the polyvinyl-alcohol copolymers of the present invention will have utility. Specific examples of aliphatic aldehydes are formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, heptanal, octanal, palmitic aldehyde, acrolein, crotonaldehyde, furfural, chloroacetaldehyde, methoxy-acetaldehyde, aminoacetaldehyde, glyoxal, glyoxylic acid, terpene aldehydes, malealdehyde, 9-isobutyl-3-carbazolealdehyde and the like. Specific examples of aromatic aldehydes include benzaldehyde, 2-naphthaldehyde, 4-methyl-benzaldehyde, 9-anthracenealdehyde, 2-hydroxybenzaldehyde, 2-chlorobenzaldehyde, aminobenzaldehyde, 2-benzaldehyde sulfonic acid, 2-benzaldehyde sulfonic acid salts, 2,4-benzaldehyde disulfonic acid, 2,4-benzaldehyde disulfonic acid salts, 4-chlorobenzaldehyde-2-sulfonic acid, 4-chlorobenzaldehyde-2-sulfonic acid salts, 4-methylbenzaldehyde-2-sulfonic acid, 4-methylbenzaldehyde-2-sulfonic acid salts, 4-hydroxybenzaldehyde-2-sulfonic acid, 4-hydroxybenzaldehyde-2-sulfonic acid salts, and the like. With respect to the above mention of salts, sodium is an example. A specific example of a terminally etherified oxyethylene aldehyde/oxaalkanal is 3,6-dioxahexanal. Butyraldehyde is a preferred aldehyde.

In this process, the random polyvinyl-alcohol/lactone copolymers starting material is acetalized to an acetalization degree of from 1.0 to 80.0 mole percent of said vinyl-alcohol units. The acetalization process may be carried out in aqueous, organic or aqueous/organic media, preferably in an aqueous medium. The acetalization reaction must be acid-catalyzed. Suitable acid-catalysts include mineral acids, such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, and the like, or organic sulfonic acids, such as methyl sulfonic acid, p-toluenesulfonic acid, and the like, or mixtures of the above. As will be appreciated by the skilled artisan, the required amount of acid catalyst will be a complex function of, for example, the chemical composition of the polyvinyl-alcohol/lactone copolymer, the chemical composition of the aldehyde components, the amount of the polyvinyl-alcohol/lactone copolymer to be used, the ash level incorporated within the polyvinyl-alcohol/lactone copolymer, the amount of the aldehyde component to be used, the acid catalyst to be used, the solvent media, and the reaction temperature. The basic requirement is that an

- effective amount of acid catalyst is required to allow the aldehyde component to condense onto the polyvinyl-alcohol/lactone copolymer. In a preferred embodiment, the acetalization reaction is performed in aqueous media with sulfuric acid catalyst at 90°C. The acid catalyst may be added at the level of 20-0.1 mole percent based on the aldehyde level to be utilized. Preferably, the acid catalyst is added at the level of 10-1 mole percent based on the aldehyde level to be utilized. When the reaction is carried out in aqueous media, the polyvinyl-alcohol/lactone copolymer is dissolved in water at a level ranging from 1 to 50 weight percent, preferably 5 to 30 weight percent. The acid catalyst may be added to the water before dissolution of the polyvinyl-alcohol copolymer, or to the aqueous solution of the polyvinyl-alcohol copolymer. The aldehyde may then be added to the solution. Alternatively, the acid catalyst may be added to an aqueous solution of the polyvinyl-alcohol copolymer and aldehyde. Additional additives such as emulsifiers may be incorporated in the reaction media.
- Examples of emulsifiers include anionic emulsifiers such as C₈ to C₂₀ alkanesulfonic acids, fluorinated fatty acids, fluorinated long chain sulfonic acids, long chain alkylsulfosuccinates, and mixtures thereof. The acetalization reaction is carried out at temperatures ranging from 0-100°C. Preferably, the reaction temperature is between 15 and 90°C.
- At the completion of the acetalization reaction, the polyvinyl-acetal/lactone copolymer of this invention is neutralized with base. The base is chosen so that it will not react with the lactone functionality. Typically, strong bases, such as alkali-metal hydroxides, should be avoided in the process. Strong bases are capable of reacting with the lactone functionality incorporated within the random polyvinyl acetal copolymers to form, for example, carboxylate ionomers or salts. Examples of bases suitable for the process include organic amines or alkali metal carbonates and bicarbonates, such as sodium bicarbonate.
- The method for isolating the random polyvinyl-acetal/lactone copolymer product of the process may depend upon the solubility of the product in the reaction medium, which in turn may depend upon the specific composition. Insoluble products may be filtered from the reaction medium, optionally washed, and dried using conventional techniques. Soluble or heavily swollen product may be precipitated by adding to the reaction medium a liquid which is miscible with the reaction medium but in which the product is insoluble. The resulting solid may be optionally washed and then dried by conventional methods.
- In a second process according to the present invention, random polyvinyl-acetal copolymers that incorporate carboxylate ionomer or salt functionalities are preferably produced by reacting, in aqueous medium, random

polyvinyl-acetal/lactone copolymers with strong bases. This process may be performed, as in previously described process, but without isolating the polyvinyl-acetal/lactone copolymer, by employing strong bases rather than weak bases for neutralization of the acid catalyst employed in the acetalization reaction.

- 5 Neutralization of the acid catalyst with a strong base leads directly to the desired random polyvinyl-acetal/carboxylate-salt copolymers or ionomers of this invention. In an alternative embodiment, the random polyvinyl-acetal/lactone copolymer produced in the earlier process of this invention may be isolated and reacted either in a heterogeneous or homogeneous manner with a strong base
- 10 capable of converting the lactone function to a carboxylic-salt functionality. Bases suitable for use in this process include any substance which is capable of hydrolyzing the lactone moiety of the random polyvinyl-acetal/lactone copolymer to form the corresponding carboxylic acid and, in turn, is capable of neutralizing said carboxylic acid to form the anionic carboxylate ionomer or salt functionality.
- 15 Specific examples of bases include alkali metal hydroxides and alkaline earth metal hydroxides, such as sodium hydroxide, lithium hydroxide, potassium hydroxide and the like, and quaternary ammonium hydroxides, such as tetra-ethanol ammonium hydroxide, tetraethyl ammonium hydroxide and the like. The amount of base utilized in this process depends on, for example, the exact
- 20 chemical nature of the basic material and the desired degree of conversion of the lactone functionalities to the carboxylate salt or ionomer functionalities. Typically, the conversion will require approximately 0.001 to 2.0 moles of base for each mole of lactone incorporated within the random polyvinyl-acetal/lactone copolymer.

- 25 The reaction medium suitable for use in latter process may be aqueous, organic, or organic/aqueous, preferably water. The reaction medium should also capable of dissolving at least 0.001 weight percent of the base selected for use. The reaction temperature and reaction time should be sufficient to allow for the conversion of at least 5 percent of the available lactone functionality to the
- 30 carboxylate ionomer or salt. In one preferred embodiment, the random polyvinyl-acetal/lactone copolymer of this invention is added to a solution of a suitable base. In another preferred embodiment, the base is added to a mixed slurry of the lactone-containing copolymer. In still another preferred embodiment, the base is added to a solution of the polyvinyl-acetal/lactone
- 35 copolymer. The base may be added neat or dissolved in a suitable solvent. Once the desired level of conversion of lactone to carboxylate ionomer or salt has been achieved, the polymer mixture may optionally be heated to complete the dissolution of the product polyvinyl-acetal/carboxylate copolymer into the

reaction solution. For water, the polymer mixture may be heated from approximately room temperature, (20°C), to the boiling point under the reaction conditions. Preferably, the polymer mixture is heated from 40°C to 90°C. Solids content of the product in solution is from 1 to 50 weight percent, preferably 1 to 30 weight percent, of the polyvinyl-acetal/carboxylate copolymer. The random polyvinyl-acetal/carboxylate copolymer of this invention may be precipitated by adding to the reaction medium a liquid which is miscible with the reaction medium but in which the product is insoluble. The resulting solid optionally may be washed and then dried by conventional methods.

10 The following specific embodiments further illustrate the present invention.

EXAMPLES 1-9 AND COMPARATIVE EXAMPLES C1-C4

15 Solution viscosity was determined by use of a Hoesppler Precision falling-ball viscometer, Hoesppler GMBH, Germany, with a 4 weight % solids (dry basis) in aqueous solution, at 20°C. Ash level was determined by titration with hydrochloric acid of sodium acetate residue from acetic acid neutralization of the product of polyvinyl acetate hydrolysis to polyvinyl alcohol, the result being calculated for sodium oxide, dry basis.

20 The following polymers were prepared by the method outlined in U.S. Patent 3,689,469, U.S. Patent 4,747,976 and U.S. Patent 4,990,335, which are herein incorporated by reference and which outline the method to make the MMA (methyl methacrylate) and the MA (methyl acrylate) containing polymers used herein.

25 Polymer "A" was a white, granular, random copolymer which incorporated between 94.0 to 95.0 mole percent vinyl alcohol with between 5.0 to 6.0 mole percent methyl acrylate, and had a 98.0 to 99.8 mole percent hydrolysis level (dry basis). Polymer A had a solution viscosity between 15-21 centiPoise, a solution pH of between 5.0 and 7.0, and a maximum ash level of 0.7 weight percent.

30 Polymer "B" was a white, granular polyvinyl alcohol with a 99.0 to 99.8 mole percent hydrolysis level (dry basis). Polymer B had a solution viscosity between 12-15 centiPoise, a solution pH of between 5.0 and 7.0, and a maximum ash level of 0.7 weight percent.

35 Polymer "C" was a white, granular, random copolymer which incorporated between 98.1 to 98.5 mole percent vinyl alcohol with between 1.5 to 1.9 mole percent methyl methacrylate, and had a 99.0 to 99.8 mole percent hydrolysis level (dry basis). Polymer C had a solution viscosity between

24-32 centiPoise, a solution pH of between 5.0 and 7.0, and a maximum ash level of 0.7 weight percent.

Polymer "D" was a white, granular, random copolymer which incorporated between 97.2 to 97.8 mole percent vinyl alcohol with between 2.2 to 2.8 mole percent methyl methacrylate, and had a 98.0 to 99.8 mole percent hydrolysis level (dry basis). This material had a solution viscosity between 12-15 centiPoise, a solution pH of between 5.0 and 7.0, and a maximum ash level of 0.7 weight percent.

Examples 1-7 demonstrate the process to produce the polyvinyl-acetal/lactone copolymers of this invention by neutralization using weak bases of the acid catalyst employed in the acetalization. Examples 8 and 9 demonstrate the process to directly produce the polyvinyl-acetal/carboxylate copolymers of this invention by neutralization with strong base, such as sodium hydroxide or potassium hydroxide.

EXAMPLES 1-7 AND COMPARATIVE EXAMPLES C1-C3

A solution of sulfuric acid (2.00 grams, 96 weight percent in water) in water (300.00 grams) was stirred for five minutes at room temperature (23 +/- 2°C) with a slight nitrogen purge. The polymer noted in Table 1 in the amount of 50.00 grams was added to the stirred solution at room temperature. The resulting stirred white slurry was heated to 90.0°C with a slight nitrogen purge. The nitrogen purge was then shut off. To the clear, moderately viscous reaction solution at 90.0°C was added butyraldehyde, in the amount shown in Table 1, in one portion with rapid stirring. The resulting reaction mixture was stirred at 90.0 +/- 5°C for one hour. The reflux condenser was removed and the slow nitrogen purge was resumed to remove any unreacted butyraldehyde from the reaction. Sodium bicarbonate (2.30 grams) was portionwise added to the reaction mixture at 90°C with stirring. For viscous reaction mixtures care was taken to control the foaming of the reaction mixture through the addition rate of the sodium bicarbonate. After stirring 10 minutes at 90°C, an additional portion of sodium bicarbonate (4.30 grams) was added to the reaction mixture. After stirring an additional 10 minutes at 90°C, the heating was discontinued and the resulting reaction mixture was allowed to cool to room temperature. The reaction mixtures of Example 3 and Comparative Example C1 consisted of a clear, moderately viscous solution. The reaction mixtures of Examples 1, 2, 4, and 5 consisted of a heavily plasticized semi-solid in a non-viscous liquid. These reaction mixtures were precipitated in acetone (500-1000 mL), and the resulting white solids were washed three times with additional acetone (300-500 mL). The reaction mixture of Comparative Example C2 consisted of a heavily plasticized solid in a non-

viscous liquid. The non-viscous liquid was decanted off the solid, and then the solid was washed with 300 mL water. The plasticized solid was then chopped up in a blender in 500 mL acetone, and the resulting solid was washed three times with 300 mL acetone. The reaction mixtures of Examples 6 and 7 and

- 5 Comparative Example C3 consisted of a white solid in a non-viscous liquid. The liquid was decanted off the white solid, and the white solid was then washed three times with water (300 mL). All washed samples were dried in a vacuum oven (P=20 inches Hg), with a slight nitrogen purge at room temperature (23 +/- 2°C) overnight and at 80°C for 4 hours. The product yields are summarized in Table 1
10 below.

EXAMPLE 8 AND COMPARATIVE EXAMPLE C4

- A solution of sulfuric acid (2.00 grams, 96 weight percent in water) dissolved in water (300.00 grams) was stirred for five minutes at room temperature (23 +/- 2°C), with a slight nitrogen purge. The polymer noted in
15 Table 1, in the amount of 50.00 grams, was added to the stirred solution at room temperature. The resulting stirred white slurry was heated to 90.0°C with a slight nitrogen purge. The nitrogen purge was then shut off. To the clear, moderately viscous reaction solution at 90.0°C was added butyraldehyde (8.72 grams) in one portion with rapid stirring. The resulting reaction mixture was stirred at 90 +/-
20 5°C for one hour. At this stage, Comparative Example C4 consisted of a plasticized white solid in a non-viscous liquid. Example 8 consisted of a heavily plasticized solid in a non-viscous liquid. The reflux condenser was removed and the slow nitrogen purge was resumed to remove any unreacted butyraldehyde from the reaction mixture. Sodium hydroxide (1.00 gram) as added in one
25 portion to the stirred reaction mixture at 90.0°C. After 10 minutes, an additional portion of sodium hydroxide (2.15 grams) was added to the stirred reaction mixture at 90.0°C. After stirring an additional 0.10 to 0.50 hour at 90.0°C, the heating was discontinued. At this stage, Comparative Example C4 consisted of a plasticized white solid in a non-viscous liquid. Example 8 consisted of a
30 moderately viscous solution. The reaction mixtures were precipitated in acetone (500 mL) and the resulting white solids were washed twice with acetone (300-400 mL), and then dried in a vacuum oven (P=20 inches Hg) with a slight nitrogen purge at room temperature (23 +/- 2°C) overnight and at 80°C for 4 hours. The product yields are summarized within Table 1 below.

35

EXAMPLE 9

A solution of sulfuric acid (2.00 grams, 96 weight percent in water) in water (300.00 grams) was stirred for five minutes at room temperature, (23 +/- 2°C) with a slight nitrogen purge. Polymer "A" (50.00 grams) was added to the

- stirred solution at room temperature. The resulting stirred white slurry was heated to 90.0°C with a slight nitrogen purge. The nitrogen purge was then shut off. To the clear, moderately viscous reaction solution at 90.0°C was added butyraldehyde (3.49 grams) in one portion with rapid stirring. The resulting
- 5 reaction mixture was stirred at 90.0 +/- 3°C for one hour. The reaction mixture consisted of a plasticized white solid in a non-viscous liquid at this stage. The reflux condenser was removed, and the slow nitrogen purge was resumed to remove any unreacted butyraldehyde from the reaction mixture. Potassium hydroxide (2.00 grams, 85 weight percent purity) was added in one portion to the
- 10 stirred reaction mixture at 90°C. After stirring 10 minutes, an additional portion of potassium hydroxide (3.19 grams, 85 weight percent purity) was added to the reaction mixture. After stirring an additional 10 minutes at 90°C, the heating was discontinued, and the resulting reaction mixture was allowed to cool to room temperature. At this stage, the reaction mixture consisted of a viscous, opaque
- 15 solution with entrained bubbles. The reaction solution was precipitated in acetone (500 mL), and the resulting white solid was washed three times with acetone (500 mL). The resulting white solid was dried in a vacuum oven (P=20 inches Hg), with a slight nitrogen purge at room temperature (23 +/- 2°C), overnight and at 80°C for four hours. The product yield is reported within Table 1 below.
- 20 It is known in the art that the acid catalyzed condensation of aldehydes with polyvinyl alcohols typically is performed in greater than 80 mole percent yield based on the amount of aldehyde condensed onto the polyvinyl alcohol and the amount of aldehyde added to the reaction. For Example, U.S. Patent No. 2,422,754 discloses the sulfuric-acid-catalyzed condensation of
- 25 butyraldehyde with polyvinyl alcohol to form polyvinyl butyrals. This reaction condenses 90 mole percent of the supplied butyraldehyde. By extrapolation of that art, the resins produced in the present invention are taken to have greater than 80 mole percent of the supplied aldehyde condensed onto the final product.

TABLE 1
Polyvinyl Acetal Polymers

Example No.	Polymer	Amount of Butyraldehyde (grams)	Product Yield (grams)
1	A	1.74	51.85
CI	B	3.49	49.05
2	C	3.49	48.80
3	D	3.49	48.69
4	A	3.49	52.25

C2	B	8.72	50.21
5	A	8.72	50.00
6	A	17.44	65.45
C3	B	26.16	57.70
7	A	26.16	69.38
C4	B	8.72	41.84
8	A	8.72	55.71
9	A	3.49	53.00

EXAMPLES 10-39 AND COMPARATIVE EXAMPLES C5-C17

- The solubility of the polymers of Examples 1-9 and Comparative Examples C1-C4 was determined in neutral and slightly basic aqueous solution.
- 5 In each of the following examples, 5.00 grams of the polymer sample indicated in Table 2 were slurried in a solution prepared by dissolving in base, in the amount indicated in Table 2, into 95.00 grams of water. Sodium hydroxide (NaOH) was ACS Reagent Grade (>97% purity) and potassium hydroxide (KOH) was ACS Reagent Grade (>85% purity). The resulting polymer mixture was mixed at $35 \pm$
- 10 0.2°C for 1 hour and then allowed to cool to room temperature ($24 \pm 2^\circ\text{C}$) and settle. The mixture was then filtered through a stainless steel wire mesh filter (200 mesh US Standard Size). Approximately 10 g of the resulting solids-free solution was weighed to a precision of 0.1 mg, as noted below in Table 2, and placed into a tared aluminum pan and dried for 1 hour at a temperature of 140°C .
- 15 The resulting dried sample was allowed to cool to room temperature in a dessicator box with calcium sulfate as the dessicant and was then reweighed. The "percent warm water solubles" was then determined. Each datum in Table 2 represents the average of two determinations.

TABLE 2
Water Solubility Results

Example	Polymer Example	Amount of Base (g)	Base	Determination 1		Determination 2		Average Solids (wt.%)	Average Warm Water Soluble (%)
				Solution Weight (g)	Solid Weight (g)	Solution Weight (g)	Solid Weight (g)		
10	1	None		10.3553	0.4241	10.2430	0.4099	4.05	80.98
11	1	0.08	NaOH	10.3155	0.4295	10.2001	0.4263	4.17	82.09
12	1	0.17	NaOH	10.4532	0.4639	10.2509	0.4560	4.45	86.07
13	1	0.25	NaOH	10.4828	0.4907	10.2120	0.4779	4.68	89.14
14	1	0.40	KOH	10.2527	0.4814	10.3676	0.4859	4.70	87.04
C5	C1	None		10.1506	0.3147	10.1854	0.3166	3.11	62.09
15	2	None		10.3388	0.2527	10.3366	0.2524	2.44	48.86
C6	C1	0.08	NaOH	10.2004	0.3209	10.3518	0.3238	3.14	61.81
16	2	0.08	NaOH	10.4084	0.4268	10.4993	0.4348	4.12	81.10
17	3	None		10.2827	0.3580	10.4102	0.3650	3.50	69.88
18	3	0.08	NaOH	10.3056	0.3803	10.4260	0.3891	3.71	73.03
C7	C1	0.17	NaOH	10.4238	0.3001	10.4411	0.2990	2.87	55.51
19	3	0.17	NaOH	10.1834	0.4377	10.3965	0.4495	4.32	83.56
20	4	None		10.2382	0.2929	10.2148	0.2952	2.88	57.51
21	4	0.08	NaOH	10.2149	0.3923	10.4507	0.3986	3.83	75.39
22	4	0.17	NaOH	10.2444	0.4328	10.2246	0.4330	4.23	81.82
C8	C1	0.25	NaOH	10.3713	0.3498	10.2578	0.3463	3.38	64.38
23	4	0.25	NaOH	10.1237	0.4493	10.2562	0.4565	4.45	84.76
C9	C1	0.40	KOH	10.1483	0.3602	10.1636	0.3585	3.54	65.56
24	4	0.40	KOH	10.3975	0.5088	10.1671	0.4990	4.90	90.74
C10	C2	None		10.3784	0.0204	10.3423	0.0203	0.20	3.93
25	5	None		10.3746	0.2437	10.4987	0.2566	2.40	47.93
C11	C2	0.08	NaOH	10.4072	0.0513	10.1480	0.0499	0.49	9.65
26	5	0.08	NaOH	10.1890	0.3553	10.2456	0.3587	3.50	68.90
C12	C2	0.17	NaOH	10.2524	0.0686	10.3234	0.0658	0.66	12.77
27	5	0.17	NaOH	10.5126	0.4452	10.3824	0.4420	4.25	82.21
C13	C2	0.25	NaOH	10.2978	0.1097	10.3556	0.1105	1.07	20.38
28	5	0.25	NaOH	10.1148	0.4749	10.2524	0.4805	4.70	89.52
29	6	None		10.1922	0.0008	10.2355	0.0013	0.01	0.21
30	6	0.08	NaOH	10.3912	0.0368	10.8600	0.0395	0.36	7.09
31	6	0.17	NaOH	10.6271	0.0854	10.4152	0.0868	0.82	15.86
32	6	0.25	NaOH	10.2678	0.1218	10.2739	0.1256	1.21	23.05

C14	C3	None		10.1724	0.0005	10.3893	0.0003	0.004	0.08
33	7	None		10.6629	0.0001	10.0810	0.0001	0.001	0.02
34	7	0.08	NaOH	10.1524	0.0483	10.2903	0.0487	0.48	9.45
35	7	0.17	NaOH	10.2360	0.0714	10.4520	0.0740	0.71	13.73
C15	C3	0.25	NaOH	10.4944	0.0803	10.3703	0.0791	0.77	14.67
36	7	0.25	NaOH	10.1303	0.0776	10.2754	0.0804	0.78	14.86
C16	C4	None		10.3255	0.0195	10.1651	0.0188	0.19	3.74
C17	C4	0.25	NaOH	10.4453	0.0843	10.1074	0.0829	0.82	15.53
37	8	None		10.1912	0.3196	10.5082	0.3305	3.15	62.81
38	8	0.25	NaOH	10.3262	0.4531	10.3047	0.4561	4.41	84.00
39	9	None		10.2637	0.3615	10.1111	0.3560	3.52	70.43

Table 3 below shows that at relatively high and at relatively low levels of acetalization, there appeared to be little or no effect of lactone on polymer solubility. All samples were dissolved in water at ca. pH=7. At low levels of acetalization, the hydroxy-acetal copolymer was highly soluble, and the solubility was unaffected (or even adversely affected) by the incorporation of lactone up to ca. 6%. On the other hand, at high levels of acetalization, the resulting polymer was so insoluble that incorporation of up to 6% lactone was ineffectual in improving solubility.

10

TABLE 3
Effect of Lactone on Water Solubility at High and Low Acetalization

Example No.	Polymer Example	Lactone (%) (approx.)	Butyraldehyde Level (g)	% Soluble
15	2	1.5	3.49	49
17	3	2.5	3.49	70
20	4	6	3.49	58
C5	C1	None	3.49	62
29	6	6	17.4	0.21
33	7	5	26.2	0.02
C14	C3	None	26.2	0.08

Table 4 below shows that at intermediate levels of acetalization, the incorporation of lactone caused dramatic improvements in water solubility.

TABLE 4
Effect of Lactone at Intermediate Acetalization

Example No.	Polymer Example	% Lactone	Butyraldehyde Level (g)	% Soluble
25	5	6	8.72	48
C10	C2	None	8.72	3.9

Table 5 below shows that the addition of a strong base to a lactone-containing polyvinyl acetal greatly increases the water solubility of the polymer.

TABLE 5
Effect of Base on Water Solubility of Example 1 Polymer

Example No.	Base (g)	% Soluble
10	None	81.0
11	0.08 NaOH	82.1
12	0.17 NaOH	86.1
13	0.25 NaOH	89.1
14	0.40 KOH	87.0

Table 5 above shows that hydrolysis to the carboxylate of a 6% lactone containing polyvinyl acetal at acetalization levels less than 2 mole % improves water solubility by ca. 10%.

Table 6 below shows a stronger effect of base on water solubility when the acetalization level was 3 to less than 7 mole %, even in samples wherein the mole % carboxylate was smaller. The solubility improvement ranged from ca. 20-60%.

TABLE 6
Effect of Base on Water Solubility at 3 < mole % Acetal < 7

Example No.	Polymer Example	Base (g)	% Lactone	% Soluble
15	2	None	1.5	48.9
16	2	0.08 NaOH	1.5	81.1
17	3	None	2.5	69.9
18	3	0.08 NaOH	2.5	73.0
19	3	0.17 NaOH	2.5	83.6
20	4	None	5	57.5
21	4	0.08 NaOH	5	75.4
22	4	0.17 NaOH	5	81.8
23	4	0.25 NaOH	5	84.8
24	4	0.40 KOH	5	90.7

Table 7 below shows effects similar to those in Table 6 at acetalization of approximately 7 mole %. The magnitude of the effect at this higher acetal level was close to 100%.

5

TABLE 7
Effect of Base on Water Solubility at ca. 7 mole % Acetal

Example No.	Polymer Example	Base (g)	% Lactone	% Soluble
25	5	None	5	47.9
26	5	0.08 NaOH	5	68.9
27	5	0.17 NaOH	5	82.2
28	5	0.25 NaOH	5	89.5

Table 8 below shows the effects of base at acetalization levels of approximately 10 mole %. Here the effect was 10,000%.

TABLE 8
Effect on Water Solubility at ca. 10 mole % Acetal/Ex. 6 Polymer

Example No.	Base (g)	% Soluble
29	None	0.21
30	0.08 NaOH	7.1
31	0.17 NaOH	15.9
32	0.25 NaOH	23.1

10

Table 9 below shows the effects of base at acetalization levels of approximately 30%. Here the effect was ca. 70,000%.

TABLE 9
Effect on Water Solubility at ca. 30 mole % Acetal/Ex. 7 Polymer

Example No.	Base (g)	% Soluble
33	None	0.02
34	0.08 NaOH	9.45
35	0.17 NaOH	13.7
36	0.25 NaOH	14.9

15

As seen in Table 6 above, the addition of base to lactone-containing polyvinyl-acetal polymer at approximately 3 to less than 7 mole % acetal resulted in improvement of water solubility by 20-60%. Table 10 below shows the effect of added base to polyvinyl acetal at the 3 to less than 7 mole % acetalization level but with no lactone incorporated. When the lactone functionality was missing, no effect of added base beyond experimental error was observed.

20

TABLE 10
Effect of Base on Water Solubility 3 < mole % Acetal <7/C1 Polymer

Example No.	Base (g)	% Soluble
C5	None	62.1
C6	0.08 NaOH	61.8
C7	0.17 NaOH	55.5
C8	0.25 NaOH	64.4
C9	0.40 KOH	65.6

Table 11 below similarly shows the effect of added base on the solubility of polymers at approximately 10 mole % acetal which contain no lactone functionality, compared with the results in Table 7 at the same level of acetalization but wherein lactone functionality was incorporated. In Table 11 there was a ca. 500% improvement in solubility of non-lactone containing polymer with added base, but the overall solubility was only ca. 25% that in Table 7.

10

TABLE 11
Effect on Water Solubility at ca. 10 mole % Acetal/C2 Polymer

Example No.	Base (g)	% Soluble
C10	None	3.93
C11	0.08 NaOH	9.65
C12	0.17 NaOH	12.8
C13	0.25 NaOH	20.4

Table 12 below shows the effect of added base on the solubility of polyvinyl acetal polymers at approximately 30 mole % acetal that contain no lactone functionality, compared with the results in Table 9 at the same level of acetalization but wherein lactone functionality was incorporated. The data in Tables 9 and 12 exhibit the same magnitude of effect and solubility. Thus, at high levels of acetalization, the effect of added base was the same regardless of whether there was or was not lactone functionality in the polymer.

15

TABLE 12
Effect on Water Solubility at 30% Acetal/C3 Polymer

Example No.	Base (g)	% Soluble
C14	None	0.08
C15	0.25 NaOH	14.7

An effect similar to that seen in Tables 8 and 12 is not observed when one examines the data on samples which were converted directly to carboxylate during neutralization of the acid catalyst. Example 37 exhibited 2000% greater solubility than did comparative example C16. Base added to the polymer of Example 37 gave Example 38 with ca. 30% higher solubility. Similarly base added to C16 to give C17 gave ca. 400% greater solubility, but still much less than Example 37 or 38.

EXAMPLES 40-60 AND COMPARATIVE EXAMPLES C18-C19

In the following examples, infrared spectroscopic evidence of the formation of ionomer from lactone is presented.

Polymer solutions were prepared as described below. The amount of base, as noted in Table 13, was dissolved in water (45.00 grams). In all but Example 56, wherein the base was potassium hydroxide, the base was sodium hydroxide. To this mixed solution at room temperature (23 +/- 1°C) was added the polymer (5.00 grams), as noted in Table 13. The resulting mixture was allowed to mix at room temperature for 5 minutes and was then heated to 85 +/- 5°C in a constant temperature water bath for 2 +/- 1 hours. The resulting polymer solutions were then allowed to cool to room temperature. Some solutions contained a small amount of undissolved solids, which were removed by filtration or other means.

Films were prepared by casting the above noted solutions onto a glass plate treated with TEFLON dry lubricant maintained at a temperature of 52.5 +/- 2.5°C with a 15 mil knife gap. The resulting films were dried on the plate for 30 minutes at 52.5 +/- 2.5°C and then further dried in a vacuum oven (P=20 inches Hg), with a slight nitrogen purge at room temperature (22 +/- 2°C), overnight and at 80°C for 4 hours. The resulting dry films were stripped off the glass plate and stored in a dessicator box with calcium sulfate as the dessicant.

Infrared analysis was performed on the above prepared films with a Nicolet 710 FT-IR spectrometer. Special note was taken with infrared peaks at between 1725-1750 wavenumbers (cm⁻¹) and at between 1550-1575 (cm⁻¹). The infrared peak at between 1725-1750 (cm⁻¹) has been attributed in the prior art to the lactone function derived from the hydrolysis of the methyl acrylate or methyl

methacrylate functions. The infrared peak at between 1550-1575 (cm^{-1}), has been attributed in the prior art to the carboxylate ionomer or salt form derived from the base opening of the above mentioned lactone functions derived from the methyl acrylate or methyl methacrylate functions, followed by neutralization of the as-formed carboxylic acid. Typically, all samples demonstrated a small infrared peak at between 1550-1575 (cm^{-1}), which has been attributed within the prior art as residual sodium ash contained within the polymer. The infrared results are summarized in Table 13 below.

TABLE 13
Infrared Analysis of Films

Example No.	Polymer Example Number	Base	Infrared Peaks at 1725-1750 (cm^{-1})	Infrared Peaks at 1550-1575 (cm^{-1})	Film Weight (g)	Water Temp (C)	Film Dissolution Time (min.)
40	1	None	++++	++	0.0178	19.7	0.33
41	1	0.08	++	++++	0.0493	19.9	0.85
42	1	0.17	0	++++	0.0347	19.8	0.30
43	1	0.25	0	++++	0.0391	19.8	0.43
C18	C1	None	0	+	0.0301	20.0	6.07
C19	C1	0.25	0	+	0.0304	21.0	1.18
44	2	None	++++	+	0.0297	20.3	1.28
45	2	0.08	+	+++	0.0509	20.4	1.40
46	3	None	++++	+	0.0406	20.5	1.28
47	3	0.17	0	++++	0.0395	20.4	0.93
48	4	None	++++	+	0.0141	19.5	0.25
49	4	0.08	+++	+++	0.0389	20.0	0.20
50	4	0.17	+	++++	0.0583	20.0	0.67
51	4	0.25	0	++++	0.0257	19.8	0.77
52	5	None	++++	++	0.0223	19.4	0.40
53	5	0.08	+	+++	0.0466	20.2	0.62
54	5	0.17	0	++++	0.0552	21.2	0.73
55	5	0.25	0	++++	0.0296	19.5	0.70
56	5	0.41	0	++++	0.0524	21.4	1.22
57	6	0.25	0	++++	0.0265	19.5	1.88
58	7	0.25	0	++++	0.0253	20.2	3.93
59	8	None	+++	++++	0.0271	22.9	0.45
60	9	None	++	++++	0.0260	22.8	0.37

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++++ denotes a very large peak
+++ denotes a large peak
++ denotes a moderately sized peak
+ denotes a small peak
0 denotes no peak

I claim:

1. A random polyvinyl-acetal copolymer comprising from about 90 to about 99 mole percent vinyl-alcohol repeat units and from about 1 to about 10 mole percent lactone functionalities, with an acetalization degree of from 1 to 80 percent of the vinyl-alcohol repeat units.
2. A random polyvinyl-acetal copolymer exhibiting improved water solubility comprising from about 90 to about 99 mole percent vinyl-alcohol repeat units and from about 1 to about 10 mole percent lactone functionalities, with an acetalization degree of from 2 to 10 percent of the vinyl alcohol units.
3. A random polyvinyl-acetal copolymers comprising from about 90 to about 99 mole percent vinyl alcohol repeat units and from about 1 to about 10 mole percent carboxylate-salt functionalities, with an acetalization degree of from 1 to 80 percent of the vinyl alcohol units.
4. A random polyvinyl-acetal copolymers exhibiting improved water solubility comprising about 90 to about 99 mole per cent vinyl-alcohol units and from about 1 to about 10 mole percent carboxylate-salt functionalities, with an acetalization degree of between 2 and 25 percent of the vinyl-alcohol repeat units.
5. A process for making random polyvinyl-acetal copolymers comprising from about 90 to about 99 mole percent vinyl-alcohol repeat units and from about 1 to about 10 mole percent lactone functionalities, with an acetalization degree of from 1 to 80 percent of the vinyl alcohol units, which process comprises mixing and reacting, in a liquid medium, a polyvinyl-alcohol/lactone copolymer with an aldehyde in the presence of an acid catalyst at a temperature in the range of 0 to 100°C, followed by neutralization of the catalyst in a weakly alkaline solution, followed by isolation of the product.
6. A process for making a random polyvinyl acetal copolymer comprising from about 90 to about 99 mole percent vinyl-alcohol repeat units and from about 1 to about 10 mole percent carboxylate-salt functionalities, with an acetalization degree of from about 1 to about 80 percent of the vinyl-alcohol repeat units, which process comprises mixing and reacting, in a liquid medium, a polyvinyl-alcohol/lactone copolymer with an aldehyde in the presence of an acid catalyst at a temperature in the range of 0 to 100°C, followed by neutralization of the catalyst in a strongly alkaline solution, followed by isolation of the product.
7. The process of Claim 5 or 6 wherein the lactone is formed from the combination of an alcohol with an adjacent lower alkyl ester or diester selected from the group consisting of methyl acrylate, ethyl acrylate, propyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, dimethyl maleate,

diethyl maleate, dipropyl maleate, dimethyl fumarate, diethyl fumarate, dipropyl fumarate, and mixtures thereof.

8. The process of Claim 5 or 6 wherein the ester is methyl methacrylate, methyl acrylate, or mixtures thereof.

5 9. The process of Claim 5 or 6 wherein the aldehyde is selected from the group consisting of aliphatic aldehydes, aliphatic-aromatic aldehydes, aromatic aldehydes, terminally etherified oxyethylene aldehydes/oxaalkanal, and mixtures thereof.

10. The process of Claim 5 or 6 wherein the aldehyde is butyraldehyde.

10 11. The process of Claim 5 or 6 wherein the liquid medium is water.

12. The process of Claim 5 or 6 wherein the acid catalyst is selected from the group consisting of sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, methyl sulfonic acid, p-toluenesulfonic acid, and mixtures thereof.

13. The process of Claim 11 wherein the polyvinyl-alcohol/lactone
15 copolymer is dissolved prior to reaction at a concentration of 1 to 50 weight percent.

14. The process of Claim 11 wherein the polyvinyl-alcohol/lactone copolymer is dissolved prior to reaction at a concentration of 5 to 30 weight percent.

20 15. The process of Claim 5 or 6 wherein the reaction temperature is in the range of 15 to 90°C.

16. The process of Claim 5 wherein the alkaline solution is selected from the group consisting of organic amines or alkali metal carbonates and bicarbonates.

25 17. The process of Claim 6 wherein the alkaline solution is selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxide.

18. A process for making random polyvinyl acetal copolymers comprising
30 from about 90 to about 99 mole percent vinyl-alcohol repeat units and from about 1 to about 10 mole percent carboxylate-salt functionality, with an acetalization degree of from about 1 to about 80 percent of the vinyl alcohol units, comprising contacting with strong alkali a random polyvinyl-acetal copolymer comprising
35 from about 90 to about 99 mole percent vinyl-alcohol repeat units and from about 1 to about 10 mole percent lactone and having an acetalization degree of from about 1 to about 80 percent of the vinyl-alcohol repeat units.

19. The process of Claim 18 wherein the base is selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/17527

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F8/28 C08F216/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 647 660 A (DAICEL CHEMICAL INDUSTRIES, LTD.) 12 April 1995 see the whole document	1-4, 18
A	US 2 306 071 A (J. G. MCNALLY) 22 December 1942 see claims 1-13	1
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A	FR 2 123 419 A (UCC) 8 September 1972 see claims 1-6	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/US 96/17527

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/17527

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